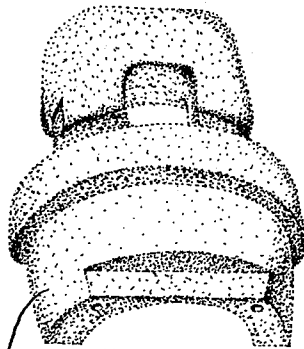


Oct. 29, 1963

A. T. PETERS ETAL
PREPARATION OF FOUNDRY CORES

3,108,340

Filed March 10, 1958



Foundry core fabricated from urea-formaldehyde bonded sand composition set by an inorganic acid gas containing sulfur or a halogen.

INVENTORS.
Adolph T. Peters
Robert G. LaValley
BY *Jerome Rudy*
ATTORNEY

1

3,103,340

PREPARATION OF FOUNDRY CORES

Adolph T. Peters, Midland, and Robert G. La Valley, Saginaw, Mich., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware
Filed Mar. 10, 1958, Ser. No. 720,179
9 Claims. (Cl. 22-193)

This invention contributes to the foundry art and has particular reference to the preparation and provision of sand cores (and molds) useful for the casting of metals and other materials wherein said structures are desired to be produced with accurately controlled dimensional tolerances. More particularly, the present invention has reference to a new and useful technique for hardening cores and molds produced from silica sand mixes containing urea-formaldehyde resins as binders. The invention also relates to an improved method for casting metals, particularly non-ferrous metals, in molds fabricated in accordance with the present invention.

Synthetic urea-formaldehyde resins are well known binder materials for foundry sands. They have been employed for this purpose, particularly when it is desired to fabricate cores, as well as certain mold structures, having good dimensional tolerances. In the usual practice, especially when cores and molds for sand casting of non-ferrous metals are being made, there is incorporated in the sand a binder of the urea-formaldehyde resin, a cereal additament of the conventional variety and water. The usual cereal binders that are used and the purposes of their utilization are explained by H. W. Dietert at pages 101-103 of his book entitled "Foundry Core Practice," 2nd Ed., published by the American Foundrymen's Society (1950). They are also discussed at page 156 of "Principles of Metal Casting," by R. W. Heine and P. C. Rosenthal, McGraw-Hill Book Co., Inc. (1955). In addition to the resin binder and cereal, small quantities of various inhibitor additives, depending upon the particular metal being cast may also be employed in the compositions. Thus, a small amount of clay sand (bentonite) may be added to develop greater green strength. Along with these, a core oil, such as a paraffin or mineral oil, may be incorporated to aid in reducing stickiness of the sand in the green state. The refractory mixture is then baked at temperatures up to 400° F., after having been fabricated into the desired shape for periods of time up to two hours or so in order to develop the requisite hardness and strength needed for the casting operation.

While the normal urea-formaldehyde/cereal bonded cores and molds are extensively employed, there are certain disadvantages attendant their utilization. For example, such compositions frequently generate excessive gas during the metal casting operation. In addition, it is a frequent experience that metal-retaining structures fabricated from such compositions are not readily shaken or removed from the casting after solidification of the metal therein or the reagent. A further disadvantage which is frequently encountered is that many cores are so shaped as to require the utilization of expensive dryer accessories to support the core during the baking operation.

There has in recent years been developed an improved method for the utilization of aqueous solutions of sodium silicate as a binder in sand compositions suitable for fabrication of foundry molds and cores. This method, which is already well known, is generally referred to as the carbon dioxide (CO₂) process. The CO₂ process permits cores and molds to be made with a mixture of sand and an aqueous solution of sodium (or other alkali metal) silicate and hardened in very short order by passing carbon dioxide gas through the wet composition after it has been fabricated into a desired shape. The gas combines chem-

2

ically with the silicate binder of the sand composition to form a silicic acid gel which cements the sand grains together and accomplishes the desired binding in periods of time that may be as short as several seconds. Sodium (and other alkali metal) silicate bonded cores and molds that have been made by the CO₂ process can be used for metal casting very soon after the gassing of the fabricated structures. The CO₂ process has been described at page 33 of "Modern Castings" for August 1956 and at page 111 of "Steel" for August 6, 1956.

The major disadvantage encountered in the employment of silicate bonded sand compositions in foundry molds and cores, including those that have been prepared by the CO₂ process, is that of poor collapsibility after the metal has been poured in and solidified in the mold. This is especially true when non-ferrous metals are being cast. In contrast to organic binders, sodium (and other alkali metal) silicate does not burn out at low temperatures. To the contrary, it sinters with the sand, especially at higher temperatures, to form glasses. As a consequence, collapsibility and shake-out features are generally very poor and frequently inadequate in sand molds and cores bonded with sodium silicate and the like and the castings may be disadvantageously difficult to remove. In addition, sodium silicate bonded cores are also prone to generate considerable gas during the casting operation. This gives rise to undesirable "blows" in the casting. Besides, the sodium silicate bonded structures are quite hygroscopic and when baked, as frequently is the case, form sodium salts which have only a low refractory quality and cause thermoplasticity.

It would be an advantage and would meet a long-sought need of the foundry art to provide a method for producing cores and molds using urea-formaldehyde binders which is less time consuming and more economical than conventional practice while being capable of yielding dimensionally accurate bonded structures that have the desirable combination of properties needed for mold and core fabrication, which structures do not generate excessive gas on metal casting while having excellent collapsibility so as to be adapted to be readily shaken from the casting after solidification of the metal. Such accomplishments would be of salient benefit for present day casting requirements, especially when thin wall structures are being fabricated wherein the mentioned features, particularly dimensional accuracy, are practical desiderations of great importance.

It is the principal object of the present invention to provide urea-formaldehyde bonded sand compositions that are capable of being fabricated into excellent quality foundry molds and cores having high strength and excellent characteristics and features, excellent dimensional characteristics and significant and substantial freedom from generation of gas during the metal casting process.

It is an associated object of the present invention to provide bonded sand compositions of the indicated variety that are adapted, during the preparation of molds and cores therefrom, to be hardened in the core box so as to maintain dimensional tolerances and to have little, if any, tendency to hygroscopicity after baking.

Another object of the invention is to provide an improved process for casting metals in and with molds and cores made of the urea-formaldehyde bonded sand compositions prepared in accordance with the present invention.

Yet a further object of the invention is to facilitate the casting of thin wall structures, especially with non-ferrous metals, by virtue of cores (and molds) possibilitated by practice of the present invention.

These and corollary objects and associated benefits and advantages may be achieved by practice of the present

invention which comprises uniformly incorporating in a foundry sand composition for the preparation of cores and molds a minor proportion of a urea-formaldehyde resin binder; fabricating the resin-containing composition in the shape of a desired core or mold (advantageously in a core or mold box); and subsequently passing through the fabricated composition an inorganic acid gas comprised of and containing sulfur or a halogen of atomic number from 9 to 35 (i.e., fluorine, chlorine, bromine) until the sand mixture is solidified and hardened by the action of gas. The solidification or hardening usually occurs in an almost instantaneous manner, after which the core (or mold) may be removed from the box or other container in which it has been hardened and used for the desired metal casting purpose. It may be advantageous in certain instances to flush the hardened core with air or other inert gas to dispose of the excess acid gas which may remain therein. This tends to avoid problems of odor or toxicity prior to further handling of the fabricated structure. While cores or molds hardened in the indicated manner can be used directly for casting after the gassing operation, they may optionally be baked, if desired, in the conventional manner to further increase their tensile strength. While such baking is not an absolute necessity for the realization of satisfactory results, it oftentimes is found to be a beneficial expedient. In any event, even when the gassed structures are baked, the time that is required for baking is generally found to be decreased by at least a third in comparison to the conventional requirements for baking when structures that are not prepared in accordance with the invention are being made.

While a variety of inorganic acid gases may be utilized in the practice of the present invention, it is generally preferable to use such gases as sulfur dioxide (SO₂), elemental chlorine (Cl₂), hydrogen chloride (HCl), hydrogen bromide (HBr), boron trichloride (BCl₃), boron trifluoride (BF₃) and the like in the practice of the invention.

The usual conventional urea-formaldehyde resins may be employed as binders for the sand in the practice of the present invention. Such resins, as are well known to those skilled in the art, may contain from about 1.5 to 2.5 (preferably about 1.8 to 2.0) moles of formaldehyde to each mole of urea therein. The resins employed are condensed in the conventional manner with an alkaline catalyst (NaOH) until they have attained a water-soluble condition. The urea-formaldehyde resins are discussed by Dietert, supra, at page 95, and by Heine and Rosenthal, supra, at page 156. They are also defined at pages 908-910 of "Organic Chemistry," by Fieser and Fieser, D. C. Heath and Co., Boston (1944).

Of course, as will be appreciated by those who are skilled in the art, the present invention is also capable of being successfully practiced with other resin binders in place of the urea-formaldehyde resins, such as resins of urea with other aldehydes or with the conventional and well known phenol-formaldehyde or other phenol-aldehyde resin binders for the sand.

The usual quantities of the urea-formaldehyde resin may be employed in the sand compositions as a binder. For example, amounts of the resin between about 0.25 and 8 or 10 percent by weight of the dry sand, preferably on the order of from 1 to 4 percent by weight, based on the weight of the dry sand in the composition, may advantageously be utilized in the compositions to be set and hardened by the acid gases. For economy's sake it is desirable to use as small a quantity of resin as may be found adequate to secure the desired strength in the final structure. While the resin can be mixed dry with the sand, a small amount of water is generally employed along with the resin in order to obtain a wet sand mixture with the aqueous resin solution. As a matter of fact, it is customary for about 3 percent by weight or so of moisture to be present in the resulting mixture. A typical mixing procedure for formulating the compositions of the inven-

tion is as follows, using a conventional Baker-Perkins muller for the compounding:

	Minutes
Mull sand plus water, if any	1
5 Add resin and mull ^a	2
Add solid additives, ^b if any, and mull	1
Add liquid additives, ^c if any, and mull	2

^a The resin can be added all dry or all liquid or partially dry and partially liquid. It is most convenient, however, to add an aqueous solution of the resin.

^b Such as inhibitors, etc., as hereinafter referred to. This step omitted in absence of such additives.

^c Such as glycols and polyglycols, as hereinafter referred to. This step omitted in absence of such additives.

Any ordinary sand or other refractory material may be employed in the practice of the invention. Advantageously, the sand or its equivalent that is employed has a fineness in accordance with the values proposed by the American Foundrymans Society (AFS) that is in the numerical range between about 25 and 180. Such sands, for example, as the types which are known as Berkeley Float sand, Juniata sand, Lake sand, Muskegon Bank sand, Vassar sand, Wedron sand, Gratiot Bank sand and the like are quite suitable. It is frequently desirable in the practice of the present invention to use clean sand, although an unwashed sand may be employed. In many cases it may be more advantageous to utilize sand having an AFS fineness number from about 50 to 125. Very frequently sands that have an AFS fineness number less than 100 may be preferable for many foundry core and mold making operations. The screen analysis of a typical suitable sand for foundry core use is included in the following tabulation, using Gratiot Bank sand (AFS 65) for the illustration:

Mesh size, U.S. Standard sieve series	Percentage by weight of sand retained on screen	Mesh size, U.S. standard sieve series	Percentage by weight of sand retained on screen
6	0	70	32.0
12	0	100	27.9
20	0.34	140	13.0
30	0.98	200	4.16
40	3.94	270	0.89
50	15.18	Pan	0.32

Other additives may also be incorporated with benefit in the resin-bonded sand compositions of the present invention, although satisfactory operation does not depend upon their employment. Thus oxidation-inhibitors for certain metals may be employed, such as sulfur and KBF₄ to prevent molten magnesium from forming oxides by reacting with moisture in the air or sand. Of course, such ingredients are not necessary for casting aluminum or brass. Likewise, glycols and water-soluble polyglycols may be employed to increase the baked strength of the cores that are baked after gassing. Boric acid may also be employed to improve the physical properties of the structures as well as to reduce the dwell time of the structures after gassing, i.e., the interval after gassing during which the core or other structure becomes fully hardened. In addition, acrylamide polymers, such as polyacrylamide, may be utilized to improve the separation of the hardened structure from the container in which it is fabricated as well as to minimize the stickiness of the sand composition and render it easier to handle.

The resin-containing sand mixture, prior to the gassing, may be fabricated to the desired shape in any suitable manner. Thus, the mixtures may be applied directly to the forming surfaces for the mold or core by manual or mechanical ramming, or by pneumatic spraying or distributing apparatus, or by otherwise pressing the material into the shaping space or cavity provided therefor. Advantageously, the required form or shape of core or mold may be produced using a pattern, core box or equivalent means. When core boxes or the like are utilized, they

5

may be provided with apertures or passageways to permit flow of the acid gas into the said mixture. In addition, holes or passageways for gas flow may also be provided within the fabricated mass of resin containing sand in order to facilitate distribution of the acid gas therethrough.

The quantity of the acid gas employed and the gassing time utilized depends on the resin content of the sand mixture being set and the size of the mold or core being fabricated. Suitable quantities of the gas as well as adequate gassing times can be readily determined by the skilled worker following simple and straightforward tests. Generally, too short a gassing time will cause an undesirably soft core or mold structure to be obtained. Overgassing, however, produces no deleterious effect in the fabricated structure and has no other harmful influence, other than being an uneconomical practice. The proper quantity of gas and length of time for gassing can ordinarily be gaged from results obtained with a standard compression sample having a diameter of about two inches and a length equal to the diameter prepared from sand containing about 2 percent of the urea-formaldehyde binder. When such a sample is gassed with SO₂ for about one second while passing the acid gas through the sample under a pressure of about 20 pounds per square inch gauge (p.s.i.g.), a set hardening effect is generally obtained within about one second. The gassing can be accomplished conveniently at room temperature although, if desired, lower or higher temperature conditions can also be utilized.

Further illustration of the invention is manifest in the following examples which are intended to be merely demonstrative and not limiting, wherein all parts and percentages are to be taken by weight.

Example 1

A series of sand mixtures of washed Gratiot Bank sand was thoroughly mixed with an aqueous solution of urea-formaldehyde resin containing about 50 percent solids. The resin had a formaldehyde to urea mole ratio of about 1.8:1. Each of the mixtures also contained about one percent sulfur and ½ percent KBF₄. The resin-containing mixtures were fabricated into standard core forms of about two inches in length by two inches in diameter which were cured by passing sulfur dioxide gas through them under about 20 p.s.i.g. until hardened. For purposes of comparison, some of the cores were baked after the gassing operation by placing them in an oven for 20 minutes at 325° F. For purposes of additional comparison, cores were prepared according to the CO₂ process using 4 percent Na₂SiO₃ as a binder and CO₂ under 15 pounds pressure for 20 seconds for curing. The results are set forth in the following tabulation, wherein Samples "A" and "B" were prepared in accordance with the invention and Sample "X" is the core prepared following the CO₂ process. In the table, the compression and tensile strengths refer to results obtained with standard tests for such properties. The hardness is measured on the smooth side of the core with a Dietert No. 673 Dry Hardness Tester. In this test, the instrument is pressed down on the specimen. The maximum hardness reading on a hard surface would be 100 units.

Sample	AFS of fineness of sand	Percent resin solids in mixture	Gas	Gassing time in seconds	Compression (C) strength, p.s.i.		Tensile (T) strength, p.s.i.		Hardness (H)		Retained strength ¹		
					As gassed	Baked	As gassed	Baked	As gassed	Baked	C	T	H
"A"-----	65	1.5	SO ₂	20	280+	280+	32	67	80	75	0	0	0
"B"-----	130	3	SO ₂	30	280+	280+	14	140	85	86	108	20	25
"X"-----	65	2.4	CO ₂	20	220	280+	30	130	80	85	280+	39	79

¹ In order to determine retained strength, the cores were gassed as indicated; then baked for 20 minutes at 325° F., then additionally baked for an hour at 650° F. As is obvious, lower retained strengths are a reliable measure of greater collapsibility and better shakeout characteristics.

² Na₂SiO₃.

Each of the cores had excellent dimensional tolerances. Cores and molds prepared in accordance with the inven-

6

tion similar to those set forth in the foregoing were found to be well adapted for use in the successful casting of magnesium according to conventional techniques and to provide excellent results in the finished castings. The castings obtained were precisely formed and had excellently smooth surface finishes, due to the substantial freedom from blowing of the bonded sand structures. After the casting, the collapsibility and shakeout characteristics of the core forms prepared according to the invention were found to be excellent. Commensurate good results are obtained when casting aluminum and brass or other nonferrous metals with the cores and molds of the invention. Suitable ferrous castings can be similarly prepared. The sulfur and KBF₄ are not employed for aluminum, brass or iron castings. A foundry sand core fabricated from a urea-formaldehyde bonded sand composition and hardened in accordance with the present invention is illustrated in the sole FIGURE of the hereto annexed drawing.

Example 2

An AFS 65 Muskegon Bank sand was mixed with 1 percent sulfur, 0.5 percent KBF₄, 0.5 percent diethylene glycol and 2 percent of the same urea-formaldehyde resin (in 50 percent aqueous solution) as employed in Example 1. Cores of the type described in the first example had the following properties after 20 seconds of gassing with SO₂ under 20 p.s.i.g.

	Initial strengths (p.s.i.)	Baked strengths (p.s.i.) 20 min. at 325° F.	Retained strengths (p.s.i.) 30 min. at 325° F., 60 min. at 650° F.
C-----	146	280+	28
T-----	22	340	<10
H-----	70	93	<10

Example 3

The following resin-containing sand composition was intimately mixed, formed into cores, and gassed for 3 minutes with BCl₃ under 20 p.s.i.g.

	Parts
Gratiot Bank sand (AFS 65) -----	94.5
Sulfur -----	1
KBF ₄ -----	0.5
50 percent aqueous solution of urea-formaldehyde resin having 1.8:1 aldehyde to urea mole ratio----	4

The properties of the gassed cores were as follows:

	Initial strengths (p.s.i.)	Baked strengths (p.s.i.) 25 min. at 325° F.	Retained strengths (p.s.i.) 25 min. at 325° F., 60 min. at 650° F.
C-----	280+	280+	68
T-----	25	185	<10
H-----	75	80	15

Example 4

Several compositions basically similar to that set forth

in Example 3 were prepared excepting to add increasing proportions of diethylene glycol to sequential samples

and to gas the fabricated cores with SO₂ as in Example 1. The results were as follows:

Percent of glycol in composition	Initial strengths, p.s.i.		Baked strengths, p.s.i. 20 min. at 325° F.	
	T	H	T	H
0 (blank).....	48	72	119	65
0.25.....	33	80	235	81
0.50.....	32	85	291	50
0.75.....	20	70	340	92
1.00.....	12	45	275	95
1.50.....	10	20	125	90

Example 5

The procedure of Example 4 was duplicated with compositions containing ½ percent of the glycol and increasing resin binder contents. The results were as follows:

Percent aqueous resin solution in composition	Initial strengths, p.s.i.		Baked strengths, p.s.i. 25 min. at 250° F.	
	T	H	T	H
4.....	29	75	300	91
5.....	45	82	310	93
6.....	52	90	365	95

Example 6

The procedure of Example 4 was duplicated excepting to replace the glycol additive with varying quantities of boric acid (H₃BO₃) in the several samples and to gas the cores for only 15 seconds. The results were as follows:

Percent of boric acid in composition	Initial strengths, p.s.i.		Baked strengths, p.s.i. 20 min. at 325° F.	
	T	H	T	H
0 (blank).....	48	72	119	65
1.....	73	85	250	93
2.....	72	83	238	92
3.....	68	80	242	92

In addition, use of the boric acid in the compositions decreased the dwell time from at least 240 seconds for the blank to 210 seconds for 1 percent H₃BO₃; 60 seconds for 2 percent H₃BO₃; and 70 seconds for 3 percent H₃BO₃. Such reductions in dwell time permits efficient handling of large size cores that would otherwise be extremely difficult, if not totally impossible, to fabricate.

What is claimed is:

1. Method for fabricating foundry cores and molds from silica sand compositions which comprises mixing said sand with between about 0.25 and 10 percent by weight, based on the weight of the dry sand in the com-

position, of a resin binder consisting essentially of a water-soluble synthetic urea-formaldehyde resin in which the mole ratio of formaldehyde to urea is from about 1.5 to 2.5:1, respectively; fabricating said sand mixture into a structure suited for shaping metal by casting; and hardening said sand composition by passing therethrough an acid gas selected from the group consisting of inorganic halogen acid gases of halogens of atomic number from 9 to 35 and sulfur dioxide gas until said structure has been solidified and hardened by the action of said gas on the resin binder.

2. The method of claim 1, wherein said sand composition is mixed with between about 1 and 4 percent by weight of said resin.

3. The method of claim 1, wherein said resin sand mixture is fabricated by being shaped in a core or mold box and is hardened by passing said acid gas therethrough while said sand composition is in said box.

4. The method of claim 1, wherein said acid gas is sulfur dioxide.

5. The method of claim 1, wherein said acid gas is elemental chlorine.

6. The method of claim 1, wherein said acid gas is boron trichloride.

7. A shaped, refractory article for metal casting as produced by the method of claim 1.

8. The method of casting metals which comprises mixing sand with a minor proportion of between about 0.25 and 10 percent by weight, based on the weight of the dry sand in the resulting composition, of a resin binder consisting essentially of a water-soluble synthetic urea-formaldehyde resin in which the mole ratio of formaldehyde to urea is from about 1.5 to 2.5:1, respectively; forming a metal retaining structure of the resulting sand composition; hardening said structure by passing therethrough an acid gas selected from the group consisting of inorganic halogen acid gases of halogens of atomic number from 9 to 35 and sulfur dioxide gas; and casting the metal in the resulting mold.

9. The method of claim 8, wherein said metal that is cast is a non-ferrous metal.

References Cited in the file of this patent

UNITED STATES PATENTS

1,482,357	Ellis	Jan. 29, 1924
1,482,358	Ellis	Jan. 29, 1924
2,229,291	Groten	Jan. 21, 1941
2,422,118	Meyer	June 10, 1947
2,528,934	Wiles	Nov. 7, 1950
2,679,490	Meiser et al.	May 25, 1954
2,723,253	Waudell	Nov. 8, 1955
2,874,428	Bonney	Feb. 24, 1959
3,008,205	Blaies	Nov. 14, 1961

FOREIGN PATENTS

710,099	Great Britain	June 9, 1954
---------	---------------------	--------------

OTHER REFERENCES

Foundry Trade Journal (publication),	May 12, 1955.
--------------------------------------	---------------